

Scandium, Yttrium, and Lanthanum Benzyl and Alkynyl Complexes with the N-(2-Pyrrolidin-1-yl-ethyl)-1,4-diazepan-6-amido Ligand

Ge, Shaozhong; Meetsma, Auke; Hessen, Bart

Published in:
Organometallics

DOI:
[10.1021/om8004228](https://doi.org/10.1021/om8004228)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Ge, S., Meetsma, A., & Hessen, B. (2009). Scandium, Yttrium, and Lanthanum Benzyl and Alkynyl Complexes with the N-(2-Pyrrolidin-1-yl-ethyl)-1,4-diazepan-6-amido Ligand: Synthesis, Characterization, and Z-Selective Catalytic Linear Dimerization of Phenylacetylenes. *Organometallics*, 28(3), 719-726. <https://doi.org/10.1021/om8004228>

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Scandium, Yttrium, and Lanthanum Benzyl and Alkynyl Complexes with the *N*-(2-Pyrrolidin-1-ylethyl)-1,4-diazepan-6-amido Ligand: Synthesis, Characterization, and Z-Selective Catalytic Linear Dimerization of Phenylacetylenes

Shaozhong Ge, Auke Meetsma, and Bart Hessen*

Center for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Received May 9, 2008

1,4,6-Trimethyl-*N*-(2-pyrrolidin-1-ylethyl)-1,4-diazepan-6-amine (HL) reacts with $M(\text{CH}_2\text{Ph})_3(\text{THF})_3$ to give the dibenzyl complexes $(\text{L})M(\text{CH}_2\text{Ph})_2$ ($M = \text{Sc}$, **1**; $M = \text{Y}$, **2**; $M = \text{La}$, **3**). Compounds **1**, **2**, and **3** can be converted to their corresponding cationic monobenzyl species $[(\text{L})M(\text{CH}_2\text{Ph})]^+$ ($M = \text{Sc}$, **Y** and **La**) by reaction with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$. Reaction of $(\text{L})\text{Sc}(\text{CH}_2\text{Ph})_2$ with 2 equiv of phenylacetylene affords the monomeric dialkynyl complex $(\text{L})\text{Sc}(\text{C}\equiv\text{CPh})_2$ (**4**), while reactions of $(\text{L})M(\text{CH}_2\text{Ph})_2$ ($M = \text{Y}$ and **La**) give the dimeric dialkynyl complexes $[(\text{L})M(\text{C}\equiv\text{CPh})(\mu\text{-C}\equiv\text{CPh})]_2$ ($M = \text{Y}$, **5**; $M = \text{La}$, **6**). The neutral complexes (**2**, **3**, **5**, and **6**) and the cationic monobenzyl species $[(\text{L})M(\text{CH}_2\text{Ph})]^+$ ($M = \text{Y}$ and **La**) are catalysts for the Z-selective linear head-to-head dimerization of phenylacetylenes. The cationic yttrium and the neutral lanthanum systems are the most effective catalysts in the series. The related scandium species show poor activity and selectivity.

Introduction

The catalytic dimerization of terminal alkynes is a straightforward and atom-economical method to synthesize conjugated enyne motifs, which are important building blocks for organic synthesis and key units found in a variety of biologically active compounds and synthetic conjugated polymers for optoelectronic applications.¹ Organo rare earth metal compounds have been reported to catalyze this transformation effectively with high selectivity.² For olefin polymerization and hydroamination/cyclization catalysis by organo rare earth compounds, it has been demonstrated that the performance of this family of catalysts is strongly influenced by the ionic radius (a uniquely tunable

parameter for the trivalent rare earth metals³), ancillary ligands, and usage of neutral versus cationic species.^{4,5} For the catalytic dimerization of alkynes, however, as yet, little is known about the influence of these parameters.

Recently, we reported a highly efficient and regioselective cationic yttrium-based catalyst for Z-selective linear dimerization of terminal alkynes, employing the *N*-(2-pyrrolidin-1-ylethyl)-1,4-diazepan-6-amido (**L**).^{2a} Here we describe the synthesis and characterization of neutral dibenzyl, dialkynyl, and cationic monobenzyl scandium, yttrium, and lanthanum complexes supported by this ligand and a comparative study of their performance in the catalytic dimerization of phenylacetylenes.

Results and Discussion

Synthesis and Characterization of Dibenzyl Complexes $(\text{L})M(\text{CH}_2\text{Ph})_2$ ($M = \text{Sc}$, **1; $M = \text{Y}$, **2**; $M = \text{La}$, **3**).** The rare earth metal tribenzyl compounds $M(\text{CH}_2\text{Ph})_3(\text{THF})_3$ have recently emerged as convenient organo rare earth metal starting materials, which are readily accessible from the reaction of rare

* Corresponding author. E-mail: B.Hessen@rug.nl.

(1) (a) Katayama, H.; Nakayama, M.; Nakano, T.; Wada, C.; Akamatsu, K.; Ozawa, F. *Macromolecules* **2004**, *37*, 13. (b) Takayama, Y.; Delas, C.; Muraoka, K.; Uemura, M.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 14163. (c) Takayama, Y.; Delas, C.; Muraoka, K.; Sato, F. *Org. Lett.* **2003**, *5*, 365. (d) Tykwinski, R. R.; Zhao, Y. *Synlett* **2002**, 1939. (e) Brønsted Nielsen, M.; Schreiber, M.; Baek, Y. G.; Seiler, P.; Lecomte, S.; Bouden, C.; Tykwinski, R. R.; Gisselbrecht, J.-P.; Gramlich, V.; Skinner, P. J.; Bosshard, C.; Günter, P.; Gross, M.; Diederich, F. *Chem.—Eur. J.* **2001**, *7*, 3263. (f) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632. (g) Ciulei, S. C.; Tykwinski, R. R. *Org. Lett.* **2000**, *2*, 3607. (h) Nicolaou, K. C.; Dai, W. M.; Tsay, S. C.; Estevez, V. A.; Wrasidlo, W. *Science* **1992**, *256*, 1172. (i) Trost, B. M. *Science* **1991**, *254*, 1471.

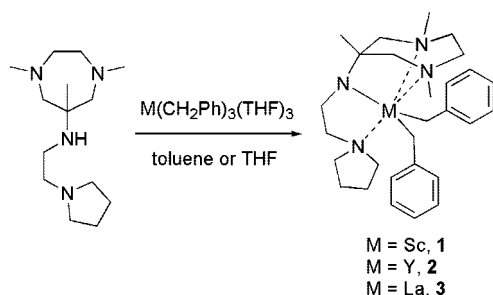
(2) (a) Ge, S.; Quiroga Norambuena, V. F.; Hessen, B. *Organometallics* **2007**, *26*, 6508. (b) Liu, Y.; Nishihira, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5592. (c) Komeyama, K.; Kawabata, T.; Takehira, K.; Takaki, K. *J. Org. Chem.* **2005**, *70*, 7260. (d) Tazelaar, C. G. J.; Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936. (e) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184. (f) Wang, J. Q.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. *Organometallics* **1999**, *18*, 2407. (g) Straub, T.; Haskel, A.; Eisen, M. *J. Am. Chem. Soc.* **1995**, *117*, 6364. (h) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931. (i) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. (j) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.

(3) (a) Anwender, R. *Top. Organomet. Chem.* **1999**, *2*, 1. (b) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(4) For olefin polymerization: (a) Gao, W.; Cui, D. *J. Am. Chem. Soc.* **2008**, *130*, 4984. (b) Bambirra, S.; van Leusen, D.; Tazelaar, C. G. J.; Meetsma, A.; Hessen, B. *Organometallics* **2007**, *26*, 1014. (c) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404. (d) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339. (e) Bambirra, S.; Bounkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182. (f) Lawrence, S. C.; Ward, B. D.; Dubberley, S. R.; Kozak, C. M.; Mountford, P. *Chem. Commun.* **2003**, 2880. (g) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075.

(5) For hydroamination/cyclization: (a) Zi, G.; Xiang, L.; Song, H. *Organometallics* **2008**, *27*, 1242. (b) Yuen, H. F.; Marks, T. J. *Organometallics* **2008**, *27*, 155. (c) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. *Dalton Trans.* **2006**, 1157. (d) Gribkov, D. V.; Hultsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748. (e) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673. (f) Lauterwasser, F.; Hayes, P. G.; Brse, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234. (g) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560.

Scheme 1. Synthesis of Compounds 1–3



earth metal trihalides $\text{MX}_3(\text{THF})_n$ with benzyl potassium.⁶ $\text{M}(\text{CH}_2\text{Ph})_3(\text{THF})_3$ reacts with 1,4,6-trimethyl-*N*-(2-pyrrolidin-1-ylethyl)-1,4-diazepan-6-amine (**HL**)^{2a} in toluene or THF to afford the dibenzyl complex $(\text{L})\text{M}(\text{CH}_2\text{Ph})_2$ ($M = \text{Sc}, \mathbf{1}$; $M = \text{Y}, \mathbf{2}$; $M = \text{La}, \mathbf{3}$) as yellow crystals after crystallization from a toluene/pentane mixture (isolated yield: 77% for **1**; 80% for **2**; 68% for **3**) (Scheme 1). When performed in C_6D_6 or $\text{THF}-d_8$, these reactions are seen by NMR spectroscopy to be quantitative. Compounds **1**, **2**, and **3** are highly air and moisture sensitive, but thermally robust and can be stored in the solid state or solution at ambient temperature without decomposition for a few months. The related yttrium dialkyl complex $(\text{L})\text{Y}(\text{CH}_2\text{SiMe}_3)_2$ ^{2a} in benzene solution gradually decomposes with release of TMS at ambient temperature. In C_6D_6 solution, the pendant pyrrolidinyl groups in these complexes are coordinated to the metal centers, as both its α - and β -H resonances are diastereotopic at ambient temperature. The benzyl methylene protons in **1**, **2**, and **3** are diastereotopic, with ^1H resonances (in benzene- d_6 at 25 °C) at δ 2.24 and 2.11 ppm ($J_{\text{HH}} = 8.4$ Hz) for **1**, δ 2.22 and 1.96 ppm ($J_{\text{HH}} = 7.1$ Hz and $J_{\text{YH}} = 2.7$ Hz) for **2**, and δ 2.34 and 2.11 ppm (J_{HH} not resolved due to fluxionality in benzene- d_6 at 25 °C; $J_{\text{HH}} = 7.5$ Hz in toluene- d_8 at –30 °C) for **3**. The corresponding ^{13}C resonances (solvent: benzene- d_6) are found at δ 52.3 ($J_{\text{CH}} = 114.8$ Hz) for **1**, δ 51.4 ppm ($J_{\text{CH}} = 120.7$ Hz and $J_{\text{YC}} = 28.2$ Hz) for **2**, and δ 62.6 ppm ($J_{\text{CH}} = 134.0$ Hz) for **3**.

Complexes **1**, **2**, and **3** were characterized by single-crystal X-ray diffraction, and their molecular structures are shown in Figure 1, 2, and 3, respectively, together with selected bond lengths and bond angles. All three complexes crystallize in space group $P\bar{1}$, and the crystals contain two independent molecules in the asymmetric unit cell, which do not differ significantly; for each compound, only one of them is explicitly discussed here. The scandium compound **1** contains two η^1 -bound benzyl groups per molecule, with $\text{Sc}(1)–\text{C}(115)–\text{C}(116) = 116.88(18)^\circ$ versus $\text{Sc}(1)–\text{C}(122)–\text{C}(123) = 112.76(17)^\circ$. Each molecule of the yttrium compound **2** contains one η^1 - and one η^2 -bound benzyl group per molecule, with $\text{Y}(1)–\text{C}(115)–\text{C}(116) = 109.67(18)^\circ$ versus $\text{Y}(1)–\text{C}(122)–\text{C}(123) = 96.60(16)^\circ$. In the lanthanum compound **3**, both benzyl groups are η^2 -bound with $\text{La}1–\text{C}115–\text{C}116 = 89.4(2)^\circ$ and $\text{La}1–\text{C}122–\text{C}123 = 93.8(2)^\circ$. The η^2 -bonding mode of the benzyl group might account for the aforementioned enhanced thermal stability of **2** versus its trimethylsilylmethyl analogue. In all compounds **1–3**, the azepine moiety of the ligands is facially coordinated, with the shortest $M–\text{N}$ distances to the amide nitrogen N13. The other

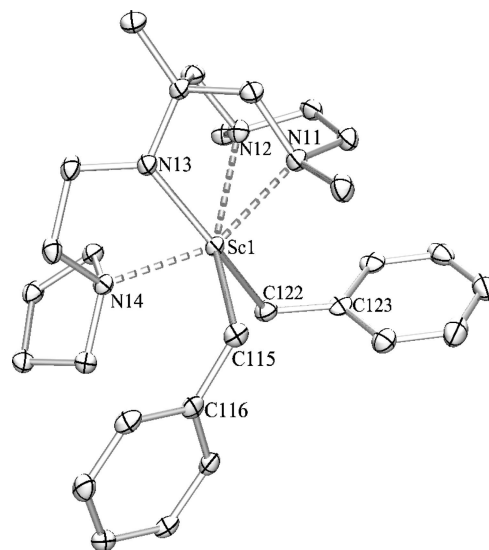


Figure 1. Molecular structure of $(\text{L})\text{Sc}(\text{CH}_2\text{Ph})_2$ (**1**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): $\text{Sc}(1)–\text{N}(11) = 2.382(2)$, $\text{Sc}(1)–\text{N}(12) = 2.585(2)$, $\text{Sc}(1)–\text{N}(13) = 2.063(2)$, $\text{Sc}(1)–\text{N}(14) = 2.362(2)$, $\text{Sc}(1)–\text{C}(115) = 2.329(3)$, $\text{Sc}(1)–\text{C}(122) = 2.368(3)$, $\text{N}(11)–\text{Sc}(1)–\text{N}(12) = 66.93(7)$, $\text{N}(11)–\text{Sc}(1)–\text{N}(13) = 77.21(8)$, $\text{N}(11)–\text{Sc}(1)–\text{N}(14) = 153.31(7)$, $\text{N}(12)–\text{Sc}(1)–\text{N}(13) = 75.33(7)$, $\text{N}(12)–\text{Sc}(1)–\text{C}(115) = 155.18(8)$, $\text{N}(13)–\text{Sc}(1)–\text{N}(14) = 76.16(8)$, $\text{N}(13)–\text{Sc}(1)–\text{C}(122) = 154.19(9)$, $\text{N}(14)–\text{Sc}(1)–\text{C}(115) = 100.05(8)$, $\text{N}(14)–\text{Sc}(1)–\text{C}(122) = 91.20(8)$, $\text{Sc}(1)–\text{C}(115)–\text{C}(116) = 116.88(18)$, $\text{Sc}(1)–\text{C}(122)–\text{C}(123) = 112.76(17)$.

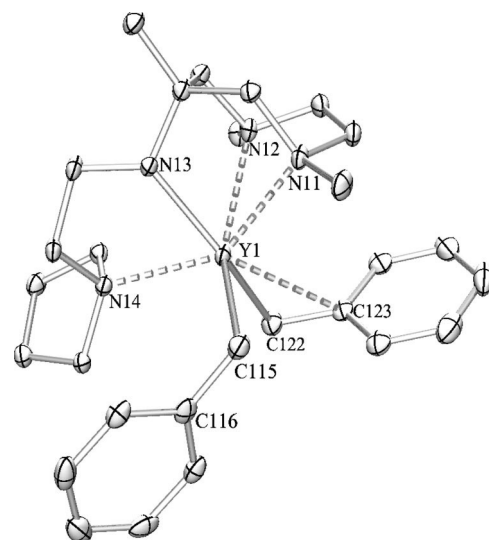


Figure 2. Molecular structure of $(\text{L})\text{Y}(\text{CH}_2\text{Ph})_2$ (**2**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): $\text{Y}(1)–\text{N}(11) = 2.524(2)$, $\text{Y}(1)–\text{N}(12) = 2.659(2)$, $\text{Y}(1)–\text{N}(13) = 2.217(2)$, $\text{Y}(1)–\text{N}(14) = 2.512(2)$, $\text{Y}(1)–\text{C}(115) = 2.491(3)$, $\text{Y}(1)–\text{C}(122) = 2.544(3)$, $\text{Y}(1)–\text{C}(123) = 3.071(3)$, $\text{N}(11)–\text{Y}(1)–\text{N}(12) = 63.81(6)$, $\text{N}(11)–\text{Y}(1)–\text{N}(13) = 73.38(7)$, $\text{N}(11)–\text{Y}(1)–\text{N}(14) = 145.31(6)$, $\text{N}(12)–\text{Y}(1)–\text{N}(13) = 72.10(7)$, $\text{N}(12)–\text{Y}(1)–\text{C}(115) = 152.35(8)$, $\text{N}(13)–\text{Y}(1)–\text{N}(14) = 72.07(7)$, $\text{N}(13)–\text{Y}(1)–\text{C}(122) = 149.54(8)$, $\text{N}(14)–\text{Y}(1)–\text{C}(115) = 102.51(8)$, $\text{N}(14)–\text{Y}(1)–\text{C}(122) = 89.85(8)$, $\text{Y}(1)–\text{C}(115)–\text{C}(116) = 109.67(18)$, $\text{Y}(1)–\text{C}(122)–\text{C}(123) = 96.60(16)$.

(6) Sc, Lu: (a) Meyer, N.; Roesky, P. W.; Bamber, S.; Meetsma, A.; Hessen, B.; Saliu, K.; Takats, J. *Organometallics* **2008**, *27*, 1501. Sc: (b) Carver, C. T.; Montreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 363. La: (c) Bamber, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454. The Y tribenzyl derivative is readily accessible via the same procedure. A full report on the structure and properties of this compound is in preparation.

two amine nitrogen atoms of the azepine moiety bind to the metal center unequally, with the differences of 0.197, 0.135, and 0.178 Å between the two $M–\text{N}(\text{amine})$ distances for **1**, **2**,

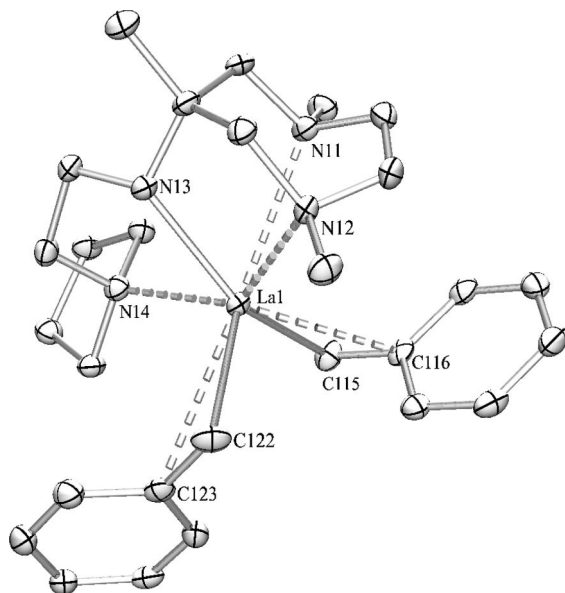
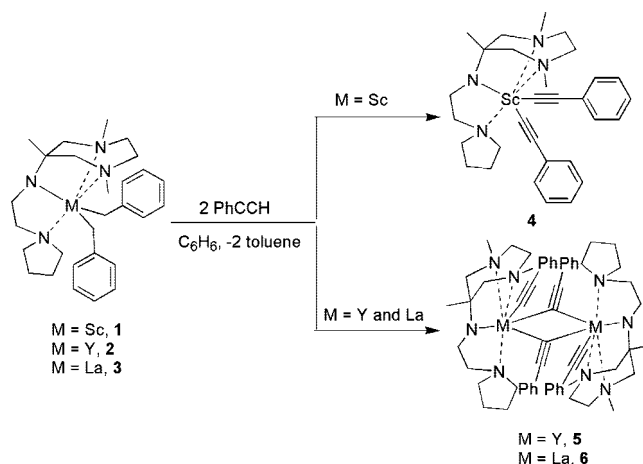


Figure 3. Molecular structure of $(\text{L})\text{La}(\text{CH}_2\text{Ph})_2$ (**3**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): $\text{La}(1)\text{--N}(11) = 2.861(3)$, $\text{La}(1)\text{--N}(12) = 2.683(3)$, $\text{La}(1)\text{--N}(13) = 2.352(3)$, $\text{La}(1)\text{--N}(14) = 2.653(3)$, $\text{La}(1)\text{--C}(115) = 2.735(4)$, $\text{La}(1)\text{--C}(116) = 3.074(4)$, $\text{La}(1)\text{--C}(122) = 2.654(4)$, $\text{La}(1)\text{--C}(123) = 3.097(4)$, $\text{N}(11)\text{--La}(1)\text{--N}(12) = 60.38(9)$, $\text{N}(11)\text{--La}(1)\text{--N}(13) = 67.42(10)$, $\text{N}(11)\text{--La}(1)\text{--N}(14) = 96.98(9)$, $\text{N}(12)\text{--La}(1)\text{--N}(13) = 69.99(10)$, $\text{N}(12)\text{--La}(1)\text{--C}(115) = 122.58(10)$, $\text{N}(13)\text{--La}(1)\text{--N}(14) = 68.69(10)$, $\text{N}(13)\text{--La}(1)\text{--C}(122) = 102.57(11)$, $\text{N}(14)\text{--La}(1)\text{--C}(115) = 87.66(10)$, $\text{N}(14)\text{--La}(1)\text{--C}(122) = 112.37(12)$, $\text{La}(1)\text{--C}(115)\text{--C}(116) = 89.4(2)$, $\text{La}(1)\text{--C}(122)\text{--C}(123) = 93.8(2)$.

and **3**, respectively. The longer $\text{M}\text{--N}(\text{amine})$ bonds are located approximately *trans* to one of the benzyl groups, as seen by the angles $\text{N}(12)\text{--Sc}(1)\text{--C}(116) = 176.26^\circ$, $\text{N}(12)\text{--Y}(1)\text{--C}(116) = 175.18^\circ$, and $\text{N}(11)\text{--La}(1)\text{--C}(123) = 169.65^\circ$. Similar asymmetries were observed previously in triazacyclononane-amide rare earth metal dialkyls.⁷

Generation of Cationic Species $[(\text{L})\text{M}(\text{CH}_2\text{Ph})]^+$. Upon reaction with 1 equiv of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the weakly coordinating polar solvent $\text{C}_6\text{D}_5\text{Br}$, the dibenzyl compounds **1**–**3** are cleanly converted to the corresponding cationic monobenzyl species $[(\text{L})\text{M}(\text{CH}_2\text{Ph})]^+$ (as seen by NMR spectroscopy) with liberation of toluene and free PhNMe_2 . The cationic monobenzyl scandium and yttrium species are sufficiently stable to allow characterization by both ^1H and ^{13}C NMR spectroscopy at ambient temperature. This is in contrast to the related yttrium dialkyl compound $(\text{L})\text{Y}(\text{CH}_2\text{SiMe}_3)_2$,^{2a} of which the corresponding cationic monoalkyl compound is insufficiently stable for characterization in the absence of a coordinating solvent like THF. The cationic monobenzyl lanthanum species in $\text{C}_6\text{D}_5\text{Br}$ decomposes within an hour at ambient temperature and precipitates as a brown oily material; after decomposition, only toluene and PhNMe_2 could be detected in solution by ^1H NMR spectrometry. The ^{13}C NMR resonances of the $\text{M}\text{--CH}_2$ groups are found at δ 54.8 ppm for $[(\text{L})\text{Sc}(\text{CH}_2\text{Ph})]^+$, δ 53.7 ppm for $[(\text{L})\text{Y}(\text{CH}_2\text{Ph})]^+$, and δ 63.1 ppm for $[(\text{L})\text{La}(\text{CH}_2\text{Ph})]^+$, showing a typical downfield shift, relative to their dibenzyl precursors

Scheme 2. Synthesis of Dialkynyl Complexes 4–6



(52.3 ppm for **1**, 51.4 ppm for **2**, and 62.6 ppm for **3**), associated with the conversion to cationic species.⁸

Stoichiometric Reactions of Compounds 1–3 with Phenylacetylene. Upon reaction with 2 equiv of phenylacetylene, the dibenzyl complex **1** is converted to the mononuclear dialkynyl scandium compound $(\text{L})\text{Sc}(\text{C}\equiv\text{CPh})_2$ (**4**) and the dibenzyl complexes **2** and **3** to the dinuclear dialkynyl compounds $[(\text{L})\text{M}(\text{C}\text{--CPh})(\mu\text{--C}\text{--CPh})_2]$ ($\text{M} = \text{Y}$, **5**; $\text{M} = \text{La}$, **6**). They were obtained as colorless crystalline material after crystallization from a toluene/hexane mixture (isolated yield: **4**, 73%; **5**, 70%; **6**, 66%) (Scheme 2). The ^{13}C resonances of $\text{M}\text{--C}(\equiv\text{C}\text{--Ph})$ are found at δ 142.1 ppm for **4**, 148.4 ppm for **5**, and 162.1 ppm for **6**. Room-temperature NMR spectra of **5** and **6** in toluene- d_8 indicate a C_s symmetrically averaged structure, and lowering the temperature to -50°C results in a decoalescence of the *o*-Ph ^1H NMR resonance for both **5** and **6**, indicating the presence of bridging and terminal alkynyl groups.

Compounds **4**–**6** were characterized by single-crystal X-ray diffraction, and the structures of **4** and **5** are shown in Figures 4 and 5, respectively (see Supporting Information for the structure of **6**), together with selected bond distances and bond angles. The structure determination of **4** at 100 K was complicated by the occurrence of a low-temperature phase transition, causing splitting of the diffraction peaks. To avoid this problem, data collection was carried out at 222 K, resulting in successful structural characterization. Compound **4** features a distorted octahedral metal center, and the coordination sphere is composed of four nitrogens of the ligand **L** and two terminal alkynyl groups with $\text{Sc}\text{--C}(15)\text{--C}(16) = 172.4(3)^\circ$ and $\text{Sc}\text{--C}(23)\text{--C}(24) = 172.3(3)^\circ$. Compounds **5** and **6** are isostructural, and only the structure of **5** is explicitly discussed here. Compound **5** is a centrosymmetric dimer with two alkynyl groups bridging the two yttrium centers. The core of the structure is a four-membered ring $\text{Y}\text{--C}(23)\text{--Y}(\text{--a})\text{--C}(23\text{--a})$, which is essentially planar (the torsion angle $\text{Y}\text{--C}(23)\text{--Y}(\text{--a})\text{--C}(23\text{--a})$ is $0.00(12)^\circ$). The azepine-amine and terminal alkynyl ligands in **5** adopt a *trans*-arrangement around the core. A *cis*-arrangement has been reported for a closely related dialkynyl complex, $\{[\text{Me}_2\text{TACN}(\text{CH}_2)_2\text{N}(\text{tBu})]\text{La}(\text{C}\equiv\text{CPh})(\mu\text{--C}\equiv\text{CPh})\}_2$.^{2d} The bridging alkynyl groups are asymmetrically bound to the two yttrium centers, with $\text{Y}\text{--C}(23) = 2.530(5)$ Å and

(7) Bambirra, S.; Boot, S. J.; van, D.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, 23, 1891.

(8) (a) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 637. (b) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522. (c) Ge, S.; Bambirra, S.; Meetsma, A.; Hessen, B. *Chem. Commun.* **2006**, 3320. (d) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2007**, 26, 5278.

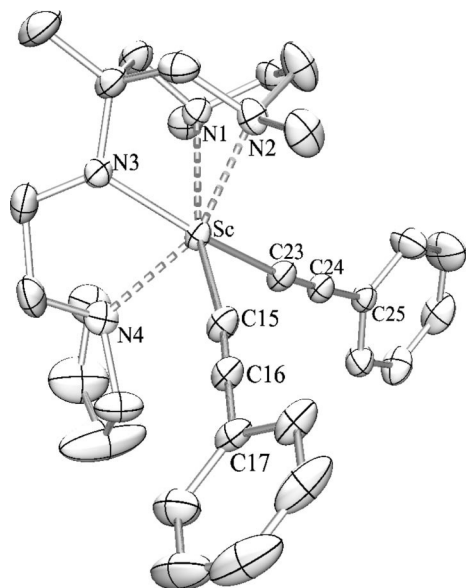


Figure 4. Molecular structure of $(\text{L})\text{Sc}(\text{C}\equiv\text{CPh})_2$ (**4**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): $\text{Sc}-\text{N}(1) = 2.485(2)$, $\text{Sc}-\text{N}(2) = 2.373(3)$, $\text{Sc}-\text{N}(3) = 2.045(2)$, $\text{Sc}-\text{N}(4) = 2.333(3)$, $\text{Sc}-\text{C}(15) = 2.262(3)$, $\text{Sc}-\text{C}(23) = 2.296(4)$, $\text{C}(15)-\text{C}(16) = 1.208(5)$, $\text{C}(23)-\text{C}(24) = 1.214(5)$, $\text{N}(1)-\text{Sc}-\text{N}(2) = 68.08(9)$, $\text{N}(1)-\text{Sc}-\text{N}(3) = 75.16(9)$, $\text{N}(1)-\text{Sc}-\text{N}(4) = 107.3(1)$, $\text{N}(1)-\text{Sc}-\text{C}(15) = 159.92(10)$, $\text{N}(2)-\text{Sc}-\text{N}(3) = 78.88(10)$, $\text{N}(2)-\text{Sc}-\text{N}(4) = 155.52(10)$, $\text{N}(3)-\text{Sc}-\text{N}(4) = 76.74(10)$, $\text{N}(3)-\text{Sc}-\text{C}(23) = 151.79(11)$, $\text{Sc}-\text{C}(15)-\text{C}(16) = 172.4(3)$, $\text{C}(15)-\text{C}(16)-\text{C}(17) = 178.7(3)$, $\text{Sc}-\text{C}(23)-\text{C}(24) = 172.3(3)$, $\text{C}(23)-\text{C}(24)-\text{C}(25) = 176.8(4)$.

$\text{Y}-\text{C}(23)-\text{C}(24) = 133.1(4)^\circ$ versus $\text{Y}(\text{a})-\text{C}(23) = 2.701(4)$ Å and $\text{Y}(\text{a})-\text{C}(23)-\text{C}(24) = 113.1(3)^\circ$. The geometry around the α -carbon ($\text{Y}-\text{C}\equiv\text{CPh}$) of the bridging alkynyl group is slightly distorted from planarity (sum of angles around $\text{C}(23)$ is 350.0°). The binding mode of terminal alkynyl groups deviates only slightly from linearity with $\text{Y}-\text{C}(15)-\text{C}(16) = 172.3(4)^\circ$. There is no significant difference in CC triple bond lengths between terminal and bridging alkynyl groups in **5** and **6**.

Catalytic Dimerization of Phenylacetylenes. Recently we have shown that the ionic catalyst $(\text{L})\text{Y}(\text{CH}_2\text{SiMe}_3)_2/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ can effectively and selectively dimerize a range of terminal alkynes to (*Z*)-1,4-disubstituted enynes.^{2a} In this contribution, dimerization of phenylacetylenes was studied with the neutral dibenzyl complexes $(\text{L})\text{M}(\text{CH}_2\text{Ph})_2$ ($\text{M} = \text{Sc}$, **1**; $\text{M} = \text{Y}$, **2**; $\text{M} = \text{La}$, **3**), the dialkynyl complexes $[(\text{L})\text{M}(\text{C}\equiv\text{CPh})(\mu-\text{C}\equiv\text{CPh})_2]$ ($\text{M} = \text{Sc}$, **4**; $\text{M} = \text{Y}$, **5**; $\text{M} = \text{La}$, **6**), and the ionic species $[(\text{L})\text{M}(\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{M} = \text{Sc}$, **Y**, **La**) as precatalysts (Scheme 3). The results are summarized in Table 1. The neutral scandium compound **1** and its corresponding dialkynyl compound **4** do not show catalytic activity toward phenylacetylene in C_6D_6 at 80°C (entry 1), but traces of *Z*-dimer and head-to-tail *gem*-dimer (2,4-diphenylbut-1-en-3-yne) are observed when the reaction mixture is heated at 120°C for 2 h. The neutral yttrium complex **2** and the neutral lanthanum complex **3** can efficiently dimerize phenylacetylene (50 equiv) to *Z*-1,4-diphenylbut-1-en-3-yne in benzene solvent with full conversion and selectivity. Compound **3**, with the larger metal (**La**), shows the higher activity of the two (entries 2 and 3). The isolated dimeric diacetylide complexes **5** and **6** dimerize phenylacetylene at identical rates to their corresponding dibenzyl precursors **2** and **3**, respectively (entries 4 and 5). The steric hindrance of an *ortho*-substituent (substrate: 2-ethynyltoluene)

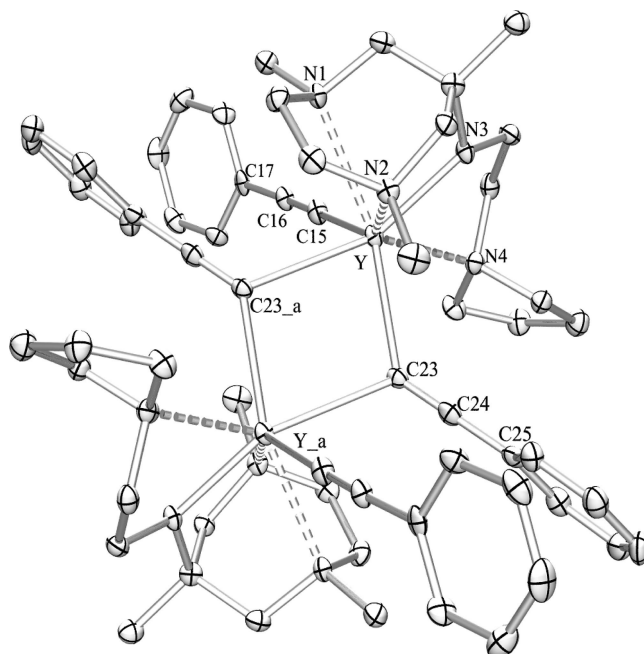
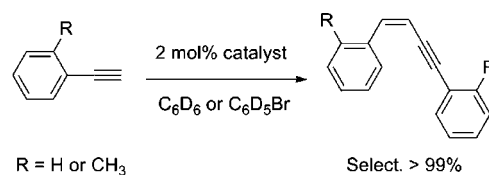


Figure 5. Molecular structure of $[(\text{L})\text{Y}(\text{C}\equiv\text{CPh})(\mu-\text{C}\equiv\text{CPh})]_2$ (**5**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): $\text{Y}-\text{N}(1) = 2.680(3)$, $\text{Y}-\text{N}(2) = 2.609(4)$, $\text{Y}-\text{N}(3) = 2.223(3)$, $\text{Y}-\text{N}(4) = 2.609(3)$, $\text{Y}-\text{C}(15) = 2.456(4)$, $\text{Y}-\text{C}(23) = 2.530(5)$, $\text{Y}(\text{a})-\text{C}(23) = 2.701(4)$, $\text{N}(1)-\text{Y}-\text{N}(2) = 62.87(9)$, $\text{N}(1)-\text{Y}-\text{N}(3) = 71.82(10)$, $\text{N}(1)-\text{Y}-\text{N}(4) = 127.93(9)$, $\text{N}(2)-\text{Y}-\text{N}(3) = 90.09(11)$, $\text{N}(2)-\text{Y}-\text{C}(15) = 146.12(14)$, $\text{N}(3)-\text{Y}-\text{N}(4) = 67.70(11)$, $\text{N}(3)-\text{Y}-\text{C}(23) = 118.19(13)$, $\text{N}(4)-\text{Y}-\text{C}(15) = 78.51(13)$, $\text{N}(4)-\text{Y}-\text{C}(23) = 81.41(12)$, $\text{Y}-\text{C}(15)-\text{C}(16) = 172.3(4)$, $\text{Y}-\text{C}(23)-\text{C}(24) = 133.1(4)$, $\text{C}(15)-\text{C}(16)-\text{C}(17) = 174.8(5)$, $\text{C}(23)-\text{C}(24)-\text{C}(25) = 179.6(4)$, $\text{C}(23)-\text{Y}-\text{C}(23_{\text{a}}) = 76.16(4)$.

Scheme 3. Catalytic *Z*-Selective Dimerization of Phenylacetylenes





shuts down the catalysis by the yttrium complex **2** (entry 9), but for the lanthanum compound **3** it only slows down the catalysis, which still proceeds to full conversion (entry 10).

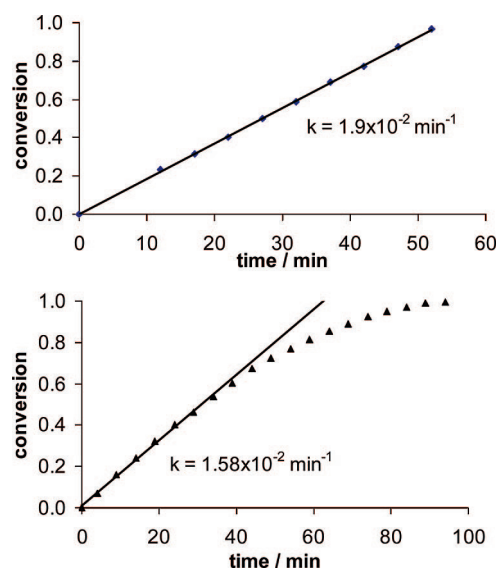
The combination of the scandium compound **1** and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ sluggishly dimerizes phenylacetylene, but two products (52% *Z*-dimer and 48% head-to-tail *gem*-dimer) are observed (entry 6). The ionic yttrium catalyst system **2**/ $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in bromobenzene (entries 7 and 11) shows the same activity with phenylacetylene and 2-ethynyltoluene as the $(\text{L})\text{Y}(\text{CH}_2\text{SiMe}_3)_2/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst reported previously.^{2a} The combination of the lanthanum complex **3** and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ only sluggishly dimerizes phenylacetylenes, but still shows *Z*-selectivity (entries 8 and 12). The thermolability of the cationic *La*-species and its poor solubility, mentioned above, may account for this low efficiency.

The kinetics of the dimerization of phenylacetylene by the two most active catalyst systems, the ionic yttrium system **1**/ $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ and the neutral lanthanum system **2**, were studied. Plots of the conversion versus time are shown in Figure 4. The catalysis by the ionic yttrium system shows a zero-order dependence on substrate concentration over the entire

Table 1. Z-Selective Dimerization of Terminal Alkynes by Yttrium and Lanthanum Catalysts

entry	Substrate	catalyst	Time (min)	conv. (%) ^b	product select. (%) ^b
1		1 or 4	60	0	
2		2	25	>99	>99
3		3	10	>99	>99
4		5	25	>99	>99
5		6	10	>99	>99
6		1/B	60	<5	52 ^c
7		2/B	5	100	100
8		3/B	30	25	>99
9		2	90	0	--
10		3	90	>99	>99
11		2/B	30	100	100
12		3/B	40	<5	>99

^a Reaction conditions: catalyst (10 μ mol), [PhNMe₂H][B(C₆F₅)₄] (B) (8.0 mg, 10 μ mol) activator where appropriate, substrate (0.5 mmol), 80 °C, solvent: C₆D₆ (0.5 mL) for neutral catalysts and C₆D₅Br (0.5 mL) for ionic catalysts. ^b Determined by in situ NMR spectroscopy. ^c 48% head-to-tail *gem*-dimer (2,4-diphenylbut-1-en-3-yne) was also formed.

**Figure 6.** Dimerization of phenylacetylene with 1/B in C₆D₅Br at room temperature (top) and with 2 in C₆D₆ at 35 °C (bottom).

conversion range. The neutral lanthanum system shows a zero-order dependence on substrate concentration only over the first 50% conversion, suggesting a change in rate-determining step at lower substrate concentrations. As yet, the precise mechanism leading to the Z-selective dimerization is unclear. Mechanistic investigations are in progress and will be reported separately.

Conclusions

The 1,4,6-trimethyl-*N*-(2-pyrrolidin-1-ylethyl)-1,4-diazepan-6-amido ligand is able to support well-defined neutral and cationic benzyl and alkynyl scandium, yttrium, and lanthanum complexes and thus is suitable as a monoanionic tetradentate ancillary ligand over the full size range of the rare earth metals.

These rare earth metal alkyl and alkynyl derivatives are active in the catalytic dimerization of phenylacetylenes. Both the metal ionic radius and the neutral or cationic nature of the catalyst species have an influence on the catalytic performance. The neutral and cationic yttrium and lanthanum complexes catalyze the linear head-to-head dimerization of phenylacetylenes with full selectivity for the Z-dimer. For yttrium, the cationic catalyst is clearly more active than its neutral precursor, but for the larger metal, lanthanum, the neutral catalyst shows the higher activity. The smallest metal in the series, scandium, not only shows the lowest catalyst activity but also lacks regioselectivity, producing both head-to-head and head-to-tail dimerization products. For practical application in the catalytic synthesis of Z-enynes, the La-system is most convenient, as it obviates the use of a fluorinated borate cocatalyst and a weakly nucleophilic polar solvent like bromobenzene. It also is less sensitive to steric hindrance in the substrate, which should allow for the widest substrate scope.

Experimental Section

General Remarks. All reactions and manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and glovebox techniques, unless mentioned otherwise. Toluene and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried over Al₂O₃ (Fluka). All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents (C₆D₆, C₇D₈, C₄D₈O; Aldrich) were vacuum-transferred from Na/K alloy, and C₆D₅Br was dried and distilled from CaH₂. NMR spectra were recorded on Varian Gemini VXR 300, Varian Gemini VXR 400, or Varian Inova 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ¹H NMR spectra were referenced to resonances of residual protons in deuterated solvents. The ¹³C NMR spectra were referenced to carbon resonances of deuterated solvents and reported in ppm relative to TMS (δ 0 ppm). Elemental analyses were performed in the Microanalysis Department of the University of Groningen, and the reported values are the average values of two independent determinations. Phenylacetylene and 2-ethynyltoluene were purchased and dried and distilled from CaH₂ prior to use. La(CH₂Ph)₃(THF)₃^{6c} and *N*-(2-pyrrolidin-1-ylethyl)-1,4-diazepan-6-amine (HL)^{2a} were prepared according to published procedures. Y(CH₂Ph)₃(THF)₃ was prepared from YCl₃(THF)_{3.5} and KCH₂Ph following the protocol for La(CH₂Ph)₃(THF)₃.

Synthesis of (L)Sc(CH₂Ph)₂ (1). A solution of HL (0.13 g, 0.52 mmol) in toluene (5 mL) was added to a solution of Sc(CH₂Ph)₃-(THF)₃ (0.24 g, 0.52 mmol) in toluene (20 mL), and the resulting mixture was stirred at room temperature for 30 min. Volatiles were removed under vacuum, and the residue was dissolved in toluene (3 mL). Pentane (5 mL) was carefully layered on top of the resulting red solution. Upon cooling to -30 °C, crystalline material formed. The mother liquor was decanted, and the solid was dried under reduced pressure, affording the title compound as a pale yellow solid (0.19 g, 0.40 mmol, 77%). ¹H NMR (500 MHz, C₆D₆, 25 °C) δ : 7.28–7.20 (8H, *o*-H + *m*-H, Ph), 6.81 (t, 2H, *J*_{HH} = 6.6 Hz, *p*-H Ph), 2.75 (m, 2H, Py α -H), 2.71 (m, 2H, NCH₂-bridge), 2.65 (m, 2H, NCH₂-bridge), 2.48 (m, 2H, NCH₂), 2.45 (d, 2H, *J*_{HH} = 12.0 Hz, CCH₂N), 2.24 (d, 2H, *J*_{HH} = 8.4 Hz, ScCH₂), 2.22 (m, 2H, Py α -H), 2.11 (d, 2H, *J*_{HH} = 8.4 Hz, ScCH₂), 2.07 (s, 6H, NCH₃), 1.70 (d, 2H, *J*_{HH} = 12.0 Hz, CCH₂N), 1.60 (m, 2H, NCH₂), 1.35 (m, 2H, Py β -H), 1.29 (m, 2H, Py β -H), 0.59 (s, 3H, CCH₃). ¹³C NMR (125.7 MHz, 25 °C, C₆D₆) δ : 155.5 (s, *ipso*-C Ph), 128.5 (d, *J*_{CH} = 151.0 Hz, *o*-C Ph), 124.4 (d, *J*_{CH} = 152.6 Hz, *m*-C Ph), 117.2 (d, *J*_{CH} = 159.3 Hz, *p*-C Ph), 74.0 (t, *J*_{CH} = 134.3 Hz, CCH₂N), 57.6 (t, *J*_{CH} = 132.2 Hz, NCH₂CH₂-azepine), 57.3 (s,

Table 2. Crystal Data and Collection Parameters of Complexes 1–3

	1	2	3
formula	C ₂₈ H ₄₃ ScN ₄	C ₂₈ H ₄₃ N ₄ Y	C ₂₈ H ₄₃ LaN ₄
fw	480.63	524.58	574.57
cryst color	yellow	yellow	yellow
cryst size (mm)	0.47 × 0.41 × 0.11	0.52 × 0.48 × 0.15	0.41 × 0.26 × 0.13
cryst syst	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	9.2415(16)	9.2345(10)	9.2008(8)
<i>b</i> (Å)	16.471(3)	16.4721(17)	16.3686(15)
<i>c</i> (Å)	17.628(3)	18.0513(19)	18.2607(17)
α (deg)	77.115(3)	75.5247(16)	75.3451(15)
β (deg)	89.025(3)	88.9232(17)	89.2363(15)
γ (deg)	82.541(3)	82.6102(17)	82.9433(15)
<i>V</i> (Å ³)	2593.4(8)	2636.5(5)	2640.1(4)
<i>Z</i>	4	4	2
ρ_{calcd} (g cm ^{−3})	1.231	1.322	1.446
μ (cm ^{−1})	3.07	22.35	16.4
<i>F</i> (000), electrons	1040	1112	1184
θ range (deg)	2.93, 26.02	3.01, 26.37	2.44, 27.49
index ranges (<i>h,k,l</i>)	±11, ±20, ±21	±11, ±20, ±22	±11, −20→21, ±23
no. of reflns collected	19 080	20 090	22 620
no. of unique reflns	9831	10 402	11 641
no. of reflns with <i>F</i> _o ≥ 4σ(<i>F</i> _o)	7551	7883	9191
w <i>R</i> (<i>F</i> ²)	0.1347	0.0851	0.0997
<i>a</i> , <i>b</i>	0.0637, 1.4677	0.0445, 0	0.0548, 0
<i>R</i> (<i>F</i>)	0.0499	0.0342	0.0390
<i>T</i> (K)	100(1)	100(1)	100(1)
GOF	1.066	1.000	1.002

Table 3. Crystal Data and Collection Parameters of Compounds 4–6

	4	5•(C ₆ H ₁₄) _{0.5}	6
formula	C ₃₀ H ₃₉ N ₄ Sc	C ₃₃ H ₄₆ N ₄ Y	C ₆₀ H ₇₈ N ₈ La ₂
fw	500.62	587.66	1189.14
cryst color	colorless	colorless	colorless
cryst size (mm)	0.39 × 0.26 × 0.23	0.39 × 0.33 × 0.28	0.22 × 0.19 × 0.16
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> (Å)	10.8798(17)	12.682(2)	13.8365(16)
<i>b</i> (Å)	12.3577(19)	14.790(3)	14.4305(16)
<i>c</i> (Å)	21.351(3)	15.914(3)	14.2150(16)
α (deg)			
β (deg)	101.561(2)	93.154(3)	92.3806(17)
γ (deg)			
<i>V</i> (Å ³)	2812.4(7)	2980.4(9)	2835.8(6)
<i>Z</i>	4	4	2
ρ_{calcd} , g cm ^{−3}	1.182	1.310	1.393
μ , cm ^{−1}	2.86	19.85	15.3
<i>F</i> (000), electrons	1072	1244	1216
θ range (deg)	2.52, 26.02	2.52, 26.02	2.46, 26.02
index ranges (<i>h,k,l</i>)	±13, ±15, −26→23	±15, −16→18, ±19	±17, ±17, ±17
no. of reflns collected	20 542	21 840	21 350
no. of unique reflns	5501	5856	5585
no. of reflns with <i>F</i> _o ≥ 4σ(<i>F</i> _o)	3133	3504	4139
w <i>R</i> (<i>F</i> ²)	0.1645	0.1216	0.0964
<i>a</i> , <i>b</i>	0.0757, 0	0.0466, 0	0.0478, 0
<i>R</i> (<i>F</i>)	0.0577	0.0492	0.0411
<i>T</i> (K)	222(1)	100(1)	100(1)
GOF	1.051	0.984	0.974

CCH₃), 57.0 (t, *J*_{CH} = 135.2 Hz, azepine-NCH₂-bridge), 52.5 (t, *J*_{CH} = 138.4 Hz, α-*C* Py), 52.3 (t, *J*_{CH} = 114.8 Hz, ScCH₂), 50.6 (q, *J*_{CH} = 136.2 Hz, NCH₃), 45.5 (t, *J*_{CH} = 129.4 Hz, Py-CH₂-bridge), 22.4 (t, *J*_{CH} = 132.0 Hz, β-*C* Py), 20.3 (q, *J*_{CH} = 125.9 Hz, CCH₃). Anal. Calc for C₂₈H₄₃N₄Sc: C, 69.97; H, 9.02; N, 11.66. Found: C, 69.50; H, 9.03; N, 11.26.

Synthesis of (L)Y(CH₂Ph)₂ (2). A solution of HL (0.28 g, 1.10 mmol) in toluene (5 mL) was added to a suspension of Y(CH₂Ph)₃-(THF)₃ (0.63 g, 1.10 mmol) in toluene (30 mL). The resulting mixture was stirred at room temperature for 30 min and then filtered. The filtrate was concentrated to about 3 mL. Pentane (5 mL) was carefully layered on top of the resulting red solution. Upon cooling to −30 °C, crystalline material formed. The mother liquor was decanted, and the solid was dried under vacuum, yielding the title compound as a pale yellow solid (0.45 g, 0.86 mmol, 80%). ¹H NMR (400 MHz, C₆D₆) δ: 7.19–7.11

(8H, *o*-*H* + *m*-*H*, Ph), 6.65 (t, 2H, *J*_{HH} = 6.4 Hz, *p*-*H* Ph), 2.89 (m, 2H, α-*H* Py), 2.82 (m, 2H, NCH₂-bridge), 2.77 (m, 2H, NCH₂-bridge), 2.51 (d, 2H, *J*_{HH} = 11.7 Hz, CCH₂N), 2.29 (m, 2H, α-*H* Py), 2.22 (dd, 2H, *J*_{HH} = 7.12 Hz, *J*_{YH} = 2.7 Hz, YCH₂), 2.01 (s, 6H, NCH₃), 1.96 (dd, 2H, *J*_{HH} = 7.12 Hz, *J*_{YH} = 2.7 Hz, YCH₂), 1.87 (m, 2H, NCH₂), 1.71 (d, 2H, *J*_{HH} = 11.7 Hz, CCH₂N), 1.48 (m, 2H, NCH₂), 1.43 (m, 2H, β-*H* Py), 1.38 (m, 2H, β-*H* Py), 0.66 (s, 3H, CCH₃). ¹³C NMR (100.5 MHz, 25 °C, C₆D₆) δ: 155.0 (s, *ipso*-C Ph), 129.8 (d, *J*_{CH} = 153.6 Hz, *o*-C Ph), 122.3 (d, *J*_{CH} = 154.4 Hz, *m*-C Ph), 116.1 (d, *J*_{CH} = 159.0 Hz, *p*-C Ph), 74.9 (t, *J*_{CH} = 133.4 Hz, CCH₂N), 59.1 (t, *J*_{CH} = 136.1 Hz, azepine-NCH₂-bridge), 57.3 (t, *J*_{CH} = 137.9 Hz, NCH₂CH₂-azepine), 57.0 (s, CCH₃), 52.6 (t, *J*_{CH} = 138.7 Hz, α-*C* Py), 51.4 (dt, *J*_{CH} = 120.7 Hz, *J*_{YC} = 28.2 Hz, YCH₂), 49.6 (q, *J*_{CH} = 127.6 Hz, NCH₃), 46.3 (t, *J*_{CH} = 126.6 Hz, Py-CH₂-bridge), 23.0 (t, *J*_{CH} = 132.4 Hz, β-*C* Py), 20.6 (q, *J*_{CH} = 124.0 Hz, CCH₃). Anal.

Calc for $C_{28}H_{43}N_4Y$: C, 64.11; H, 8.26; N, 10.68. Found: C, 64.21; H, 8.32; N, 10.35.

Synthesis of (L)La(CH₂Ph)₂ (3). To a solution of La(CH₂Ph)₃·(THF)₃ (0.898 g, 1.57 mmol) in THF (20 mL) was added dropwise a solution of ligand HL (0.0364 g, 1.57 mmol) in THF (5 mL). After completion of addition, the mixture was stirred at room temperature for 30 min. All the volatiles were removed under reduced pressure. The residue was dissolved in toluene (about 3 mL) and then filtered. *n*-Hexane (5 mL) was carefully layered on top of the filtrate. Upon cooling to $-30\text{ }^{\circ}\text{C}$, crystalline material formed, including the material suitable for single-crystal X-ray diffraction. The mother liquor was decanted, and the solid was dried under vacuum, yielding the title compound as a yellow solid (0.615 g, 1.07 mmol, 68%). ¹H NMR (400 MHz, C₆D₆) δ : 7.07 (t, 4H, $J_{\text{HH}} = 7.57\text{ Hz}$, *m*-H Ph), 6.70 (d, 4H, $J_{\text{HH}} = 7.76\text{ Hz}$, *o*-H Ph), 6.47 (t, 2H, $J_{\text{HH}} = 7.17\text{ Hz}$, *p*-H Ph), 2.88 (m, 2H, NCH₂-bridge), 2.80 (m, 2H, NCH₂-bridge), 2.67 (m, 2H, α -H Py), 2.62 (d, 2H, $J_{\text{HH}} = 12.1\text{ Hz}$, CCH₂N), 2.34 (br, 2H, LaCH₂), 2.14 (m, 2H, α -H Py), 2.11 (br, 2H, LaCH₂), 2.10 (m, 2H, NCH₂), 2.02 (s, 6H, NCH₃), 1.83 (d, 2H, $J_{\text{HH}} = 12.1\text{ Hz}$, CCH₂N), 1.63 (m, 2H, NCH₂), 1.55 (m, 2H, Py β -H), 1.42 (m, 2H, Py β -H), 0.67 (s, 3H, CCH₃). ¹³C NMR (100.5 MHz, C₆D₆) δ : 152.2 (s, *ipso*-C Ph), 131.0 (d, $J_{\text{CH}} = 153.5\text{ Hz}$, *m*-C Ph), 120.7 (d, $J_{\text{CH}} = 152.0\text{ Hz}$, *o*-C Ph), 114.3 (d, $J_{\text{CH}} = 159.4\text{ Hz}$, *p*-C Ph), 73.7 (t, $J_{\text{CH}} = 134.3\text{ Hz}$, CCH₂N), 62.6 (t, $J_{\text{CH}} = 134.0\text{ Hz}$, LaCH₂), 59.4 (s, CCH₃), 58.5 (t, $J_{\text{CH}} = 133.6\text{ Hz}$, azepine-NCH₂-bridge), 57.3 (t, $J_{\text{CH}} = 131.9\text{ Hz}$, NCH₂-azepine), 52.9 (t, $J_{\text{CH}} = 138.5\text{ Hz}$, α -C Py), 49.4 (q, $J_{\text{CH}} = 135.2\text{ Hz}$, NCH₃), 47.6 (t, $J_{\text{CH}} = 128.7\text{ Hz}$, Py-CH₂-bridge), 23.3 (t, $J_{\text{CH}} = 131.3\text{ Hz}$, β -C Py), 20.9 (q, $J_{\text{CH}} = 125.0\text{ Hz}$, CCH₃). Anal. Calc for $C_{28}H_{43}LaN_4$: C, 58.53; H, 7.54; N, 9.75. Found: C, 58.75; H, 7.60; N, 9.34.

Reaction of 1 with [PhNMe₂H][B(C₆F₅)₄]. A solution of 1 (18.7 mg, 38.9 μmol) in C₆D₅Br (0.5 mL) was added to [PhNMe₂H]-[B(C₆F₅)₄] (31.2 mg, 38.9 μmol). The resulting mixture was homogenized by agitation and transferred to an NMR tube equipped with a Teflon (Young) valve. NMR analysis indicated clean conversion to the corresponding cationic monobenzyl species, toluene, and free PhNMe₂. ¹H NMR (500 MHz, C₆D₅Br, 23 $^{\circ}\text{C}$) δ : 7.05 (t, 2H, $J_{\text{HH}} = 7.1\text{ Hz}$, *m*-H Ph), 6.65 (t, 1H, $J_{\text{HH}} = 7.2\text{ Hz}$, *p*-H Ph), 6.04 (br, 2H, *o*-H Ph), 2.82 (br, 2H, NCH₂-bridge), 2.70 (m, 2H, α -H Py), 2.63 (m, 2H, α -H Py), 2.60 (d, 2H, $J_{\text{HH}} = 12.4\text{ Hz}$, CCH₂-azepine), 2.56 (br, 2H, NCH₂-bridge), 2.15 (d, 2H, $J_{\text{HH}} = 12.4\text{ Hz}$, CCH₂-azepine), 2.06 (s, 6H, NCH₃), 1.96 (m, 2H, NCH₂-azepine), 1.87 (m, 2H, NCH₂-azepine), 1.82 (br, 2H, ScCH₂), 1.68 (m, 2H, β -H Py), 1.61 (m, 2H, β -H Py), 0.44 (s, 3H, CCH₃). ¹H ¹³C NMR (125.7 MHz, C₆D₅Br, 25 $^{\circ}\text{C}$) δ : 152.4 (s, *ipso*-C Ph), 148.5 (d, $J_{\text{CF}} = 240.7\text{ Hz}$, *o*-C C₆F₅), 138.3 (d, $J_{\text{CF}} = 235.0\text{ Hz}$, *p*-C C₆F₅), 136.5 (d, $J_{\text{CF}} = 242.9\text{ Hz}$, *m*-C C₆F₅), 133.7 (m-C Ph), 120.7 (*o*-C, Ph), 120.2 (*p*-C Ph), 124.2 (br, *ipso*-C C₆F₅), 77.3 (CCH₂N), 56.9 (azepine-NCH₂-bridge), 55.6 (NCH₂CH₂-azepine), 55.5 (s, CCH₃), 54.7 (ScCH₂), 54.0 (α -C Py), 48.7 (NCH₃), 44.9 (Py-CH₂-bridge), 21.5 (β -C Py), 18.0 (CCH₃).

Reaction of 2 with [PhNMe₂H][B(C₆F₅)₄]. A solution of 2 (19.9 mg, 37.9 μmol) in C₆D₅Br (0.5 mL) was added to [PhNMe₂H]-[B(C₆F₅)₄] (30.4 mg, 37.9 μmol). The resulting mixture was homogenized by agitation and transferred to an NMR tube equipped with a Teflon (Young) valve. NMR analysis indicated clean conversion to the corresponding cationic monobenzyl species, toluene, and free PhNMe₂. ¹H NMR (500 MHz, C₆D₅Br, 25 $^{\circ}\text{C}$) δ : 6.89 (br, 2H, *m*-H Ph), 6.48 (br, 1H, *p*-H Ph), 6.22 (br, 2H, *o*-H Ph), 2.79 (m, 2H, α -H Py), 2.63 (m, 2H, NCH₂-bridge), 2.60 (d, 2H, $J_{\text{HH}} = 11.9\text{ Hz}$, CCH₂-azepine), 2.58 (m, 2H, α -H Py), 2.49 (m, 2H, NCH₂-bridge), 2.30 (m, 2H, NCH₂-azepine), 2.13 (d, 2H, $J_{\text{HH}} = 11.9\text{ Hz}$, CCH₂-azepine), 2.09 (m, 2H, NCH₂-azepine), 2.06 (s, 6H, NCH₃), 1.65 (m, 4H, β -H Py), 1.64 (br, 2H, YCH₂), 0.59 (s, 3H, CCH₃). ¹H ¹³C NMR (125.7 MHz, C₆D₅Br, 25 $^{\circ}\text{C}$) δ : 153.4 (*ipso*-C Ph), 133.4 (m-C, Ph), 148.5 (d, $J_{\text{CF}} = 240.7\text{ Hz}$, *o*-C C₆F₅),

138.3 (d, $J_{\text{CF}} = 235.0\text{ Hz}$, *p*-C C₆F₅), 136.5 (d, $J_{\text{CF}} = 242.9\text{ Hz}$, *m*-C C₆F₅), 124.2 (br, *ipso*-C C₆F₅), 118.9 (*o*-C Ph), 118.3 (*p*-C Ph), 75.7 (CCH₂-azepine), 59.4 (NCH₂-bridge), 56.8 (CCH₃), 56.2 (NCH₂-azepine), 53.7 (br, YCH₂), 52.4 (α -C Py), 48.9 (NCH₃), 45.1 (NCH₂-bridge), 22.8 (β -C Py), 19.2 (CCH₃).

Reaction of 3 with [PhNMe₂H][B(C₆F₅)₄]. A solution of 3 (25.8 mg, 44.9 μmol) in C₆D₅Br (0.6 mL) was added to [PhNMe₂H]-[B(C₆F₅)₄] (36.0 mg, 44.9 μmol). The obtained solution was transferred to an NMR tube equipped with a Teflon (Young) valve. NMR analysis indicated clean conversion to the corresponding cationic monobenzyl species, toluene, and free PhNMe₂. ¹H NMR (500 MHz, C₆D₅Br, 23 $^{\circ}\text{C}$) δ : 6.96 (t, 1H, $J_{\text{HH}} = 7.2\text{ Hz}$, *p*-H Ph), 6.37 (t, 2H, $J_{\text{HH}} = 7.05\text{ Hz}$, *m*-H Ph), 6.21 (d, 2H, $J_{\text{HH}} = 5.92\text{ Hz}$, *o*-H Ph), 2.63 (m, 4H, NCH₂-bridge), 2.63 (d, 2H, $J_{\text{HH}} = 12.7\text{ Hz}$, CCH₂-azepine), 2.61 (m, 2H, α -H Py), 2.43 (m, 2H, α -H Py), 2.29 (m, 2H, NCH₂-azepine), 2.12 (s, 6H, NCH₃), 2.10 (d, 2H, $J_{\text{HH}} = 11.9\text{ Hz}$, CCH₂-azepine), 2.02 (m, 2H, NCH₂-azepine), 1.94 (br, 2H, LaCH₂), 1.67 (m, 2H, β -H Py), 1.63 (m, 2H, β -H Py), 0.59 (s, 3H, CCH₃). ¹H ¹³C NMR (125.7 MHz, C₆D₅Br, 23 $^{\circ}\text{C}$) δ : 148.5 (d, $J_{\text{CF}} = 240.7\text{ Hz}$, *o*-C C₆F₅), 138.3 (d, $J_{\text{CF}} = 235.0\text{ Hz}$, *p*-C C₆F₅), 136.5 (d, $J_{\text{CF}} = 242.9\text{ Hz}$, *m*-C C₆F₅), 132.1 (m-C Ph), 124.2 (br, *ipso*-C C₆F₅), 119.5 (*o*-C Ph), 114.8 (*p*-C Ph), 73.9 (CCH₂-azepine), 63.1 (LaCH₂), 59.1 (CCH₃), 57.7 (NCH₂-bridge), 56.7 (NCH₂-azepine), 52.3 (α -C Py), 48.9 (NCH₃), 46.7 (NCH₂-bridge), 23.0 (β -C Py), 20.0 (CCH₃). The *ipso*-C resonance is obscured by the solvent peaks. ¹⁹F NMR (470 MHz, C₆D₅Br, 23 $^{\circ}\text{C}$) δ : -137.1 (d, $J_{\text{FF}} = 11.5\text{ Hz}$, *o*-F), -167.3 (t, $J_{\text{FF}} = 21.3\text{ Hz}$, *m*-F), -171.2 (t, $J_{\text{FF}} = 17.8\text{ Hz}$, *p*-F).

Synthesis of (L)Sc(C \equiv CPh)₂ (4). To a solution of 1 (144.2 mg, 0.3 mmol) in toluene (35 mL) was added a solution of phenylacetylene (61.3 mg, 0.6 mmol) in toluene (2 mL). The resulting solution was stirred overnight at room temperature, and then all the volatiles were removed under vacuum. The residue was dissolved in benzene (2 mL) and hexane (1 mL) was added, followed by filtration. Upon standing at room temperature overnight, crystalline material formed, including material suitable for single-crystal X-ray diffraction. The mother liquor was decanted, and the solid was dried under reduced pressure, yielding the title compound as a white solid (110.2 mg, 0.22 mmol, 73%). ¹H NMR (400 MHz, C₆D₆, 25 $^{\circ}\text{C}$) δ : 7.65 (d, 4H, $J_{\text{CH}} = 7.68\text{ Hz}$, *o*-H Ph), 7.07 (t, 4H, $J_{\text{CH}} = 7.91\text{ Hz}$, *m*-H Ph), 6.97 (t, 2H, $J_{\text{CH}} = 7.23\text{ Hz}$, *p*-H Ph), 3.78 (m, 2H, α -H Py), 3.28 (m, 2H, NCH₂), 3.03 (m, 2H, NCH₂-bridge), 2.79 (m, 2H, NCH₂-bridge), 2.62 (d, 2H, $J_{\text{HH}} = 11.6\text{ Hz}$, CCH₂N), 2.58 (s, 6H, NCH₃), 2.32 (m, 2H, α -H Py), 2.17 (m, 2H, β -H Py), 1.91 (d, 2H, $J_{\text{HH}} = 11.6\text{ Hz}$, CCH₂N), 1.83 (m, 2H, NCH₂), 1.47 (m, 2H, β -H Py), 0.64 (s, 3H, CCH₃). ¹³C NMR (100.5 MHz, C₆D₆, 25 $^{\circ}\text{C}$) δ : 142.1 (br, ScC \equiv C-Ph), 132.0 (dt, $J_{\text{CH}} = 159.5\text{ Hz}$, $J_{\text{CH}} = 6.6\text{ Hz}$, *o*-C Ph), 128.2 (dd, $J_{\text{CH}} = 158.9\text{ Hz}$, $J_{\text{CH}} = 7.7\text{ Hz}$, *m*-C Ph), 125.7 (dt, $J_{\text{CH}} = 160.1\text{ Hz}$, $J_{\text{CH}} = 7.7\text{ Hz}$, *p*-C Ph), 102.6 (t, $J_{\text{CH}} = 4.6\text{ Hz}$, ScC \equiv CPh), 74.7 (t, $J_{\text{CH}} = 133.2\text{ Hz}$, CCH₂N), 59.6 (t, $J_{\text{CH}} = 135.6\text{ Hz}$, azepine-NCH₂-bridge), 57.8 (s, CCH₃), 57.4 (t, $J_{\text{CH}} = 137.5\text{ Hz}$, NCH₂CH₂-azepine), 54.4 (t, $J_{\text{CH}} = 139.3\text{ Hz}$, α -C Py), 51.4 (q, $J_{\text{CH}} = 135.6\text{ Hz}$, NCH₃), 45.8 (t, $J_{\text{CH}} = 128.4\text{ Hz}$, Py-CH₂-bridge), 23.1 (t, $J_{\text{CH}} = 133.0\text{ Hz}$, β -C Py), 19.5 (q, $J_{\text{CH}} = 124.8\text{ Hz}$, CCH₃). Anal. Calc for $C_{28}H_{43}N_4Sc$: C, 71.98; H, 7.85; N, 11.19. Found: C, 71.88; H, 7.89; N, 11.09.

Synthesis of [(L)Y(C \equiv CPh)(μ -C \equiv CPh)]₂ (5). A solution of 2 (104.9 mg, 0.2 mmol) in toluene (1 mL) was added to phenylacetylene (40.9 mg, 0.4 mmol), and the resulting mixture was kept for 30 min at room temperature and then at $-30\text{ }^{\circ}\text{C}$ overnight, after which crystalline material had formed. The mother liquor was decanted and the solid was dried under vacuum, giving the title compound (76.2 mg, 0.07 mmol, 70%) as a colorless solid. Crystals suitable for single-crystal X-ray diffraction were grown by crystallization from toluene/hexane. ¹H NMR (500 MHz, C₆D₆, 25 $^{\circ}\text{C}$) δ : 7.76 (br, 8H, *o*-H Ph), 7.07 (t, 8H, $J_{\text{HH}} = 7.24\text{ Hz}$, *m*-H Ph), 6.95 (t, 4H, $J_{\text{HH}} = 6.44\text{ Hz}$, *p*-H Ph), 3.54 (m, 4H, NCH₂), 3.39

(br, 8H, α -H Py), 3.13 (m, 4H, NCH₂-bridge), 3.05 (m, 4H, NCH₂-bridge), 2.83 (s, 12H, NCH₃), 2.70 (d, 4H, $J_{\text{HH}} = 11.0$ Hz, CCH₂N), 1.99 (d, 4H, $J_{\text{HH}} = 11.0$ Hz, CCH₂N), 1.98 (m, 4H, NCH₂), 1.80 (br, 8H, β -H Py), 0.75 (s, 6H, CCH₃). ¹³C NMR (125.7 MHz, C₇D₈, 25 °C) δ : 148.4 (s, C \equiv CPh), 132.1 (d, $J_{\text{CH}} = 161.6$ Hz, *o*-C Ph), 128.3 (d, $J_{\text{CH}} = 158.9$ Hz, *m*-C Ph), 126.3 (d, $J_{\text{CH}} = 160.2$ Hz, *p*-C Ph), 114.9 (br, C \equiv CPh), 77.6 (t, $J_{\text{CH}} = 135.7$ Hz, CCH₂N), 58.6 (t, $J_{\text{CH}} = 135.5$ Hz, NCH₂CH₂-azepine), 58.3 (t, $J_{\text{CH}} = 133.3$ Hz, azepine-NCH₂-bridge), 57.7 (s, CCH₃), 54.4 (t, $J_{\text{CH}} = 137.8$ Hz, α -C Py), 52.6 (q, $J_{\text{CH}} = 135.5$ Hz, NCH₃), 47.1 (t, $J_{\text{CH}} = 128.9$ Hz, Py-CH₂-bridge), 23.5 (t, $J_{\text{CH}} = 131.2$ Hz, β -C Py), 19.8 (q, $J_{\text{CH}} = 125.4$ Hz, CCH₃). The *ipso*-C resonance is obscured by the solvent peaks. Anal. Calc for C₆₀H₇₈Y₂N₈: C, 66.17; H, 7.22; N, 10.29. Found: C, 66.16; H, 7.37; N, 9.89.

Synthesis of [(L)La(C \equiv CPh)(μ -C \equiv CPh)]₂ (6). To a solution of **3** (116.4 mg, 0.2 mmol) in toluene (2 mL) was added phenylacetylene (40.9 mg, 0.4 mmol). The resulting mixture was left standing at -30 °C overnight, after which crystalline material had formed. The mother liquor was decanted and the solid was dried under vacuum, yielding the title compound as a colorless solid (72.8 mg, 65.8 μ mol, 66%). Crystals suitable for single-crystal X-ray diffraction were grown by crystallization from THF/hexane. ¹H NMR (500 MHz, C₇D₈, 25 °C) δ : 7.81 (d, 8H, $J_{\text{HH}} = 7.53$ Hz, *o*-H Ph), 7.12 (t, 8H, $J_{\text{HH}} = 7.76$ Hz, *m*-H Ph), 6.98 (t, 4H, $J_{\text{HH}} = 7.42$ Hz, *p*-H Ph), 4.12 (br, 4H, α -H Py), 3.55 (m, 4H, NCH₂), 3.16 (m, 4H, NCH₂-bridge), 3.08 (m, 4H, NCH₂-bridge), 2.83 (s, 12H, NCH₃), 2.72 (d, 4H, $J_{\text{HH}} = 11.6$ Hz, CCH₂N), 2.48 (br, 4H, α -H Py), 2.46 (br, 4H, β -H Py), 2.06 (m, 4H, NCH₂), 2.05 (d, 4H, $J_{\text{HH}} = 11.6$ Hz, CCH₂N), 1.72 (br, 4H, β -H Py), 0.73 (s, 6H, CCH₃). ¹³C NMR (125.7 MHz, C₇D₈, 25 °C) δ : 162.1 (s, C \equiv CPh), 132.2 (d, $J_{\text{CH}} = 161.3$ Hz, *o*-C Ph), 128.3 (d, $J_{\text{CH}} = 167.4$ Hz, *m*-C Ph), 126.2 (d, $J_{\text{CH}} = 162.9$ Hz, *p*-C Ph), 115.5 (br, C \equiv CPh), 76.9 (t, $J_{\text{CH}} = 132.3$ Hz, CCH₂N), 60.1 (t, $J_{\text{CH}} = 133.9$ Hz, azepine-NCH₂-bridge), 58.4 (t, $J_{\text{CH}} = 136.0$ Hz, NCH₂CH₂-azepine), 54.6 (t, $J_{\text{CH}} = 138.1$ Hz, α -C Py), 54.4 (s, CCH₃), 51.5 (q, $J_{\text{CH}} = 136.0$ Hz, NCH₃), 48.0 (t, $J_{\text{CH}} = 127.7$ Hz, Py-CH₂-bridge), 24.3 (t, $J_{\text{CH}} = 131.4$ Hz, β -C Py), 19.8 (q, $J_{\text{CH}} = 126.2$ Hz, CCH₃). The *ipso*-C resonance is obscured by the solvent peaks. Assignment of NMR resonances was aided by COSY and HSQC experiments. Anal. Calc for C₆₀H₇₈La₂N₈: C, 60.60; H, 6.61; N, 9.42. Found: C, 59.25; H, 6.59; N, 9.30. The rather low carbon content found (whereas H and N values agree with the calculated values) is likely to be due to some carbide formation. We have observed this before on a La-acetylide compound.^{2d}

Catalytic Dimerization of Phenylacetylenes by 1–6. Phenylacetylene (51.1 mg, 0.5 mmol) or 2-ethynyltoluene (58.0 mg, 0.5 mmol) was added to a solution of complex **1**, **2**, **3**, or **4** (10 μ mol) or **5** or **6** (5 μ mol) in C₆D₆ (0.5 mL). The resulting solution was transferred to an NMR tube equipped with a Teflon (Young) valve. The tube was inserted into an NMR spectrometer that was preheated to 80 °C, and a single pulse spectrum was taken every 5 min. The

final volume of the reaction mixture is approximately 550 μ L (500 μ L stock solution + ~50 μ L substrate) and [M] is ~18.2 mM.

Catalytic Oligomerization of Phenylacetylenes by the Ionic Catalysts (1, 2, or 3)/[PhNMe₂H][B(C₆F₅)₄]. In a Tomas tube, a solution of **1** or **2** (10 μ mol) in C₆D₅Br (0.5 mL) was added to [PhNMe₂H][B(C₆F₅)₄] (8.0 mg, 10 μ mol), and then the resulting solution was treated with phenylacetylene (51.1 mg, 0.5 mmol) or 2-ethynyltoluene (58.0 mg, 0.5 mmol). The resulting mixture was transferred to an NMR tube equipped with a Teflon (Young) valve. The tube was inserted into an NMR spectrometer which was preheated to 80 °C, and a single pulse spectrum was taken every 5 min. The final volume of the reaction mixture is approximately 550 μ L (500 μ L stock solution + ~50 μ L substrate) and [M] is ~18.2 mM.

Structure Determinations of Compounds 1–6. Suitable single crystals of the compounds were obtained by crystallization as described above. Crystals were mounted on a glass fiber inside a glovebox and transferred under inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were collected with Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS⁹). The structures were solved by Patterson methods, and extension of the models was accomplished by direct methods applied to difference structure factors, using the program DIRDIF.¹⁰ In a subsequent difference Fourier synthesis all hydrogen atoms were located, of which the positional and isotropic displacement parameters were refined. All refinements and geometry calculations were performed with the program packages SHELXL¹¹ and PLATON.¹² Crystallographic data and details of the data collections and structure refinements are listed in Table 2 (for 1–3) and Table 3 (for 4–6).

Acknowledgment. This investigation was financially supported by the Chemical Science Division of The Netherlands Organisation for Scientific Research (NWO-CW).

Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM8004228

(9) Sheldrick, G. M. *SADABS Version 2*, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany, 2000.

(10) Beurskens, P. T.; Beurskens, G.; De Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.

(11) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(12) Spek, A. L. *PLATON*, program for the Automated Analysis of Molecular Geometry; University of Utrecht: Utrecht, The Netherlands, 2000.